Method of refrigeration and installation for implementing the method

The invention relates to an installation and a method
5 of refrigeration using a thermochemical system,
especially for freezing various products or for
producing chilled water.

Heat generation or refrigeration installations based on
10 a liquid/gas phase change or on reversible sorption
between a gas, called the working gas, and a liquid or
solid sorbent, are known. A reversible sorption may be
an absorption of a gas by a liquid, an absorption of a
gas on a solid, or a reaction between a gas and a
15 solid. A reversible sorption between a sorbent S and a
gas G is exothermic in the synthesis direction S + G →
SG and is endothermic in the decomposition direction SG
→ S + G. In a liquid/gas phase change of the gas G,
the condensation is exothermic and the evaporation is
20 endothermic.

These reversible phenomena can be represented on a
Clausius-Clapeyron plot by their equilibrium line:

25   InP = $f(-1/T)$, more precisely InP = $-\dfrac{\Delta H}{RT}+\dfrac{\Delta S}{R}$,

P and T being the pressure and the temperature
respectively, ΔH and ΔS being the enthalpy and the
entropy of the phenomenon (decomposition, synthesis,
30 evaporation, condensation), respectively, and R being
the perfect gas constant.

The endothermic step may be advantageously employed in
an installation of this type for freezing various
35 products (especially water for obtaining ice) or for
producing chilled water.

Various reactors and methods based on these principles

have been disclosed.

EP 0 810 410 discloses a system comprising a reactor and an evaporator/condenser connected via a pipe provided with a valve. A thermochemical reaction or a solid/gas adsorption takes place in the reactor. The latter includes means for heating the solid that it contains and means for extracting the heat from the exothermic synthesis reaction, these means being formed either by a heat exchanger, or by increasing the thermal mass of the reactor. The reactor is designed in such a way that, with its content, it has a thermal mass sufficient to absorb the heat produced during the exothermic reaction. The method of managing this system consists in bringing the evaporator/condenser into communication with the reactor when the evaporator/condenser is filled with the working gas in liquid form, this having the effect of cooling the evaporator/condenser by evaporation, and then in turning on the means intended to heat the solid so as to deliver the working gas to the evaporator/condenser and to condense it therein. The means intended to heat the solid in the reactor are turned on before the previous step has been completed. The refrigeration produced by the evaporator/condenser can be used to produce chilled water or ice. However, in this system, the cycle times are relatively long because the regeneration of the system takes place at a high temperature T_h and the cooling of the reactor takes place at ambient temperature T_0. Consequently, the reactor undergoes a relatively large thermal excursion between the regeneration temperature and the ambient temperature. This results in a low performance coefficient.

EP-0 835 414 discloses a method of refrigeration and/or heat production using thermochemical phenomena involving a gas G in an installation comprising two reactors (R_1, R_2) containing a respective salt (S_1, S_2),

an evaporator for the gas G and a condenser for the gas G. The equilibrium temperature of the salt S_1 is below the equilibrium temperature of the salt S_2 at a given pressure. The reactors are placed in thermal contact so as to be able to exchange heat. The reactors, the evaporator and the condenser are brought selectively into communication with each other by means of pipes provided with valves. In the initial state, the reactors and the condenser are in communication, at the pressure of the condenser. During operation, one of the reactors is in synthesis mode while the other reactor is in decomposition mode. In this operation mode, refrigeration is achieved at a single temperature level, that is to say at the evaporation temperature in the evaporator.

The object of the present invention is to provide a method and an installation for achieving a very high refrigeration power per unit volume, for example around 200 kW/m^3, with greatly reduced cycle times and higher performance levels, especially for instantaneous and rapid production of chilled water or for the fast freezing of various products (for example for the production of ice).

According to the present invention, the method of refrigeration using a thermochemical system comprises three reversible phenomena involving the gas G in three chambers (EC), (1) and (2), the respective equilibrium temperatures $T_{E(EC)}$, $T_{E(1)}$ and $T_{E(2)}$ at a given pressure being such that $T_{E(EC)} < T_{E(2)} < T_{E(1)}$, the chambers (1) and (2) being in thermal contact. The method is distinguished by the fact that, starting from a state in which the three chambers are at ambient temperature and at the same pressure:

    - in a first step, the chamber (1) is isolated and the chambers (EC) and (2) are brought into communication in order to carry out the exothermic synthesis in (2), the heat produced being absorbed by

the chamber (1);

- in a second step, the chamber (2) is isolated and the chambers (EC) and (1) are brought into communication in order to carry out the exothermic synthesis in (1), the heat produced being absorbed by the chamber (2); and

- in a third step, the three chambers are brought into communication and thermal energy is supplied to the chamber (1) in order to carry out the exothermic decomposition steps in (1) and in (2), for the purpose of regenerating the installation, which is then left to return to the ambient temperature.

More precisely:

- during a preliminary step, the three chambers are isolated from one another and placed at the ambient temperature, said chambers containing SEC+G, S1 and S2 respectively;

- during a first step, the chambers (EC) and (2) are brought into communication, the chamber (1) remaining isolated, in order to carry out the exothermic synthesis in (2) and refrigeration in the chamber (EC) at the equilibrium temperature in (EC) corresponding to the pressure in the assembly formed by (2) and (EC);

- during a second step, the chamber (2) is isolated and the chambers (EC) and (1) are brought into communication in order to carry out the exothermic synthesis in (1) and refrigeration in the chamber (EC) at the equilibrium temperature in (EC) corresponding to the pressure in the assembly formed by (1) and (EC);

- during a third step, the three chambers are brought into communication in order to carry out the synthesis in (EC) and the decomposition in (2), and thermal energy is supplied to (1) in order to carry out the decomposition in (1); and

- during a fourth step, the three chambers are isolated and left to cool down to the ambient temperature.

The refrigeration cycle is thus complete.

The reversible phenomenon in the reactors (1) and (2) may be a reversible sorption chosen from reversible chemical reactions between the gas G and a solid, the adsorptions of the gas G on a solid, and absorptions of the gas G by a liquid.

The reversible phenomenon in the device (EC) may be a sorption, such as that defined above, or a liquid/gas phase change of the gas G. Liquid/gas phase changes are preferred as they allow refrigeration at a higher rate than with sorptions, because of the lower thermal inertia of the system.

In the rest of the text, "sorption" will denote a reversible sorption, the term "phenomenon" will denote a reversible phenomenon, chosen from sorptions and liquid/gas phase changes, the term "L/G change" will denote the liquid/gas phase change of the gas G, the terms "S1", "S2" and "SEC" will denote the sorbent in the gas-lean state or, where appropriate, G in the gaseous state, in the reactor (1), the reactor (2) and the device (EC) respectively, the terms "S1+G", "S2+G" and "SEC+G" will denote the sorbent in the gas-rich state or, where appropriate, G in the liquid state, in the reactor (1), the reactor (2) and the device (EC) respectively.

As an example of gas G, mention may be made of ammonia (NH_3) and its derivatives, hydrogen (H_2), carbon dioxide (CO_2), water (H_2O), hydrogen sulfide (H_2S), methane and other natural gases. As sorption reaction, mention may be made of reactions involving ammonium compounds (for example chlorides, bromides, iodides or sulfates), hydrates, carbonates or hydrides.

The method according to the present invention may be

implemented using an installation that comprises an endothermic component, consisting of a device (EC), and an exothermic component, consisting of a reactor (1) and a reactor (2). Said installation is distinguished by the fact that:

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- the reactors (1) and (2) are in thermal contact so that each of them constitutes an active thermal mass for the other;

- the reactors (1) and (2) and the device (EC)

10 are provided with means for bringing them selectively into communication;

- the reactor (1) and the reactor (2) are provided with heating means (6) and heat extraction means (5); and

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- at the start of the cycle:

* the reactors (1) and (2) contain a sorbent S1 and a sorbent S2, respectively, capable of participating in a reversible sorption involving a gas G, the equilibrium curve of

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the reversible sorption in (1) lying within a higher temperature range than that of the equilibrium curve of the reversible sorption in (2) in the Clausius-Clapeyron plot; and

* the device (EC) contains a compound G capable

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of undergoing a liquid/gas phase change or an SEC+G sorbent rich in gas G capable of participating in a reversible sorption, the equilibrium temperature of which is below the equilibrium temperature of the reversible

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sorption in the reactor (2).

In one particular embodiment, the thermal contact between the reactors (1) and (2) is achieved by placing the reactor (1) inside the reactor (2). For example,

35 the reactors (1) and (2) may be concentric, the reactor (1) being placed inside the reactor (2).

In another embodiment, each of the reactors (1) and (2) is formed by several hollow plates containing the

respective sorbents, plates of one of the reactors
alternating with the plates of the other. The thickness
of the plates is typically about 1 to 3 cm.

5   In an installation according to the invention,
refrigeration takes place in the device (EC). If the
refrigeration is intended for producing ice or chilled
water, the installation furthermore includes a
reservoir (3) containing water in direct thermal
10 contact with the device (EC). If it is desired to
produce ice, it is preferred to use a reservoir (3)
divided into compartments having the size of the
desired pieces of ice. When the installation is used to
manufacture chilled water, the reservoir R may be a
15 coil, incorporated into the wall of the device (EC),
water flowing through said coil. If the installation is
intended to freeze various products, the reservoir (3)
has a suitable shape for containing and freezing the
products correctly.
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Figure 1 shows a diagram of an installation according
to the invention.

In this figure, the installation comprises a reactor
25 (1), provided with heating means (6), a reactor (2), in
thermal contact with the reactor (1) and provided with
cooling means (5), a device (EC) and pipes provided
with valves V1 and V2 for bringing the reactors (1) and
(2) selectively into contact with (EC). The reactor (1)
30 contains a sorbent S1 capable of undergoing sorption
with a gas G. The reactor (2) contains a sorbent S2
capable of undergoing sorption with the gas G, the
equilibrium temperature of S1 being above the
equilibrium temperature of S2 at a given pressure. The
35 device (EC) contains the gas G in the liquid state or a
sorbent SEC capable of undergoing sorption with the gas
G, the equilibrium temperature of SEC being below the
equilibrium temperature of S2 and a given pressure. The
device (EC) is advantageously an evaporator/condenser

(noted hereinafter by evaporator) in which a liquid/gas (L/G) phase change takes place. (EC) is in direct thermal contact with a reservoir (3) incorporated into its wall and containing water.

The installation and the method according to the invention are particularly advantageous when the device (2) is an evaporator/condenser (denoted hereinafter by evaporator). In one particular embodiment, the evaporator has a structure as shown in figures 2 and 3. Figure 2 shows a cross-sectional view and figure 3 shows a longitudinal sectional view.

The evaporator consists of a cylinder (8) which is closed at its two ends and has a circular cross section. The circular cross section includes, in its upper part, a concave circular arc corresponding to the cross section of the ice tray (7). Hollow fins (9) are placed inside the evaporator, in the longitudinal direction. A tube (10) connected to the pipe for transferring the gas G between the evaporator and the reactors (1) or (2) runs into the cylindrical chamber of the evaporator via a bore made in one of the ends of the cylinder, and it is placed directly beneath the wall of the ice tray (7). The working gas G, in the form of a boiling liquid, is placed in the bottom of the evaporator. The space between the walls of the fins is occupied by the phase change material M.

The outer wall of the evaporator (8) is made of a material having a high thermal diffusivity, that is to say a low thermal capacity in order to allow the wall temperature to drop rapidly and a high thermal conductivity in order to allow rapid ice formation. A material, for example based on aluminum, which has a low thermal capacity and a high conductivity, is suitable because of its compatibility with ammonia, which is a gas frequently used in negative-temperature refrigeration installations. The fins (9) increase the

diffusion of heat, from the boiling liquid into the ice tray, and the mechanical strength of the evaporator. The ice tray 7 is provided with many transverse partitions placed so as to obtain the desired shape of the pieces of ice. The overall shape of the ice tray has a suitable toroidal half-moon shape, thereby allowing easy demolding of the pieces of ice formed.

The phase change material M placed between the walls of the hollow fins maintains the temperature of the evaporator at a low temperature. This makes it possible to extend the ice production step during the transient heating step for regenerating the reactor isolated from the evaporator.

The particular configuration of the tube (10) and its position in the chamber of the evaporator are such that the hot gases, coming from the reactor during the step 5 of bringing the high-pressure reactor into communication with the evaporator maintained at low pressure by the phase change material, firstly strike the wall of the ice tray, which makes it easier to separate the pieces of ice.

In one particular embodiment, the method of refrigeration according to the invention is implemented using an installation as described above, in which the chamber (EC) furthermore contains a solid/liquid phase change material M. The phase change material M is chosen in such a way that the solidification temperature is at least slightly below the temperature of refrigeration in (EC) corresponding to the synthesis in (2). A temperature difference of a few degrees, for example from 1°C to 10°C, is appropriate. For example, this temperature is 0°C when the desired objective is to manufacture ice. Material M may be chosen, for example, from paraffins, such as n-alkanes having from 10 to 20 carbon atoms, eutectic mixtures and eutectic solutions. The process takes place in the same manner

as in the general case described above. However, during
the regeneration step, the temperature in the chamber
(EC) is that of the melting point of the material M,
resulting in a regeneration temperature which is less
than that occurring in the absence of the change of
phase material. This alternative way of implementing
the method of the invention consequently reduces the
cycle time and the amount of energy required for
regeneration.

The implementation of the method of the invention in an
installation according to the invention is described in
greater detail below with reference to figures 4 to 7
in the case of an installation in which (EC) is an
evaporator/condenser. Figures 4 to 7 show the position
of the installation in the Clausius-Clapeyron plot
during the various steps of an operating cycle. The
curves in the plots correspond to monovariant
phenomena. The operation of the installation would,
however, be identical if a divariant phenomenon,
corresponding for example to the absorption of the gas
G by an absorbent solution (for example water/NH_3 or
water/LiBr) or to the adsorption of the gas G on the
surface of an active solid (for example active carbon
or zeolite), were to be used in the reactors (1) and/or
(2).

Initial step:

During an initial step, the components (1), (2) and
(EC) are placed at the ambient temperature T_0 and
isolated from one another by keeping the valves V1 and
V2 closed. Since the components are isolated from one
another, they are at their respective equilibrium
pressures at T_0, denoted by PE^0, $P1^0$ and $P2^0$. The
reactors (1) and (2) contain S1 and S2 respectively
while the device (EC) contains G in liquid form. S1, S2
and G are chosen in such a way that $P1^0 < P2^0 < PE^0$. The
situation of the components is shown by 1^0, 2^0 and E^0 in

the plot shown in figure 4.

Step 1: First refrigeration step

5   The valve V1 remains closed and the installation operates by means of the reactor (2) and the evaporator (EC). Opening the valve V2 equalizes the pressure (PE^1 = $P2^1$) between (EC) and (2). The evaporator (EC) passes from the position E^0 to E^1 and the reactor (2) from the

10   position 2^0 to 2^1. The change in the respective positions is shown in figure 4. In the 2^1 state, the reactor (2) is in synthesis position, whereas in the E^1 state the evaporator (EC) is in the evaporation state. Bringing (EC) into communication with (2) causes a

15   sudden drop of temperature in (EC) and the temperature passes from T_0 to T_{E1}. This temperature drop thus firstly allows rapid freezing of the water contained in a tray (not shown in figure 1) incorporated into the wall of the evaporator. A first refrigeration power

20   peak is then observed. The gas liberated by the evaporation in (EC) is absorbed by the sorbent S2 contained in (2), causing a temperature rise in the reactor (2) owing to the fact that the sorption is highly exothermic. The energy produced by the sorption

25   in (2) is absorbed by the reactor (1), which is isolated from (EC) but in thermal contact with (2). The reactor (1) therefore constitutes a thermal capacitance allowing the reactor (2) to remain far apart from its thermodynamic equilibrium. The reactor (1) then passes

30   from the position 1^0 to the position 1^1 by remaining on its thermodynamic equilibrium line.

Step 2: Second refrigeration step

35   When synthesis has been completed in the reactor (2) at the end of step 1 [the duration of which is determined by the nature and the quantities of the elements used in (2) and (EC)], the valve V2 is closed and the valve V1 immediately opened. The installation then operates

by means of the reactor (1) and the evaporator (EC). The equilibrium pressure that is established between the reactor (1) and the evaporator (EC) makes these components pass from the positions shown by E^1 and 1^1 to the positions shown by E^2 and 1^2. This change is shown in figure 5.

Refrigeration takes place in the evaporator (EC) at E^2, that is to say at a temperature T_{E2} below the refrigeration temperature T_{E1} in step 1. Since steps 1 and 2 take place one after the other, they give high levels of refrigeration power at T_{E2}, driving (EC) only from T_E^1 to T_E^2. During this step, the reactor (2) acts as a thermal capacitance for the reactor (1). The reactor (2), which absorbs the exothermic reaction heat coming from the reactor (1), rises in temperature and is at 2^2 on its thermodynamic equilibrium line. Thanks to this thermal capacitance, the reactor (1) remains at 1^2, which is a position far from its thermodynamic equilibrium. This results in a strong, second refrigeration power peak.

Step 3: Ice-separation and regeneration step

At or before the end of step 2, valve V2 is opened, the valve V1 remaining open.

The components (1), (2) and (EC) move rapidly to positions 1^3, 2^3 and C^3 at an intermediate pressure level between that of step 1 and step 2. The contents of the reactor (2) are in the decomposition position and the contents of the reactor (1) remain in the synthesis position. These synthesis/decomposition positions remain far from equilibrium because of the thermal contact that exists between the reactors (1) and (2). The result is that the decomposition in the reactor (2) is more rapid than the synthesis that emanates in the reactor (1). Thus, condensation is immediately initiated in the device (EC), which moves

rapidly to the position C^3. This exothermic condensation is possible as the heat is absorbed by the surface melting of the pieces of ice, causing them to separate and thus making it easier to subsequently remove them from the device (EC). Turning the heating means (6) on in (1) right from the start of this step (at the same time as the valve V2 is opened) results in condensation in (EC), which progressively moves from the position C^3 to a pressure level C^4 that again allows the gas G to condense. Condensation is again possible when the reactor (1) is in the position 1^4 and when the condensation pressure becomes greater than the saturation vapor pressure corresponding to the mean temperature of the cooling fluid of the element (EC) (for example that of the external air). The temperature T_1^4 is the regeneration temperature (T_{reg}) and the device (EC) is in the position C^4, which moves the reactor (2) to the position 2^4 also at the pressure level imposed by the condensation. The thermodynamic position C^4 is then necessarily such that the temperature corresponding to the position C^4 is above the ambient temperature T_0, because the heat of condensation is transferred to the heat sink. The regeneration of the device means that the heat of this exothermic condensation must be extracted from a heat sink, which may be the ambient air or a cooling circuit. The change in the position of the various components is shown in figure 6.

Step 4: Cooling step and return to the initial step

Once the regeneration of the reactors (1) and (2) has been completed, the valves V1 and V2 are closed. The reactors thus isolated are then cooled, either naturally or using cooling means (5) (fan, cooling circuit, etc.), lowering the temperature and the pressure. Each component moves along its thermodynamic equilibrium curve until it reaches the ambient temperature and thus returns to the initial position,

E^0, 1^0 and 2^0 respectively. The device is thus under the initial conditions of the refrigeration storage step at the start of the operating cycle. The change in position of the various components during this step is shown in figure 7.

When the method of the invention is employed with an installation in which the chamber (EC) furthermore includes a phase change material M, the phase change temperature T_M of which is at least slightly below the refrigeration temperature T_{E1} in (EC) corresponding to synthesis in (2), the regeneration of the sorbents contained in the reactors (1) and (2) is more rapid. The successive states in which the reactors (1) and (2) and the chamber (EC) are found during the successive steps are illustrated in the Clausius-Clapeyron plot shown in figure 8. In this embodiment, the device (EC) may have the configuration shown in figures 2 and 3.

Initial step:

This is similar to the initial step described above. The components (1), (2) and (EC) are in the positions shown by 1^0, 2^0 and E^0 in figure 8.

Step 1: First refrigeration step

The valve V1 remains closed. The installation operates by means of the reactor (2) and the evaporator (EC). Opening the valve V2 equalizes the pressure ($PE^1 = P2^1$) between (EC) and (2). The evaporator (EC) passes from the position E^0 to E^1 and the reactor (2) passes from the position 2^0 to 2^1. In the 2^1 state, the reactor (2) is in the synthesis position, while in the E^1 state the evaporator (EC) is in the evaporation state.

Bringing (EC) into communication with (2) causes a sudden drop in the temperature (EC), which passes from T_0 to T_{E1}. This temperature drop thus firstly results in

rapid cooling and then partial freezing of the water contained in the tray 7 incorporated into the wall of the evaporator, then solidification of the material M. The gas released by the evaporation in (EC) is absorbed by the sorbent S2 contained in (2), which results in a temperature rise in the reactor (2) because the sorption is highly exothermic. The energy produced by the sorption in (2) is absorbed by the reactor (1), which is isolated from (EC) but in thermal contact with (2). The reactor (1) therefore constitutes a thermal capacitance allowing the reactor (2) to remain far from its thermodynamic equilibrium. The reactor (1) then passes from the position 1^0 to the position 1^1, remaining on its thermodynamic equilibrium line.

Step 2: Second refrigeration step

The presence of a phase change material in (EC) does not modify the execution of step 2. After this step, the reactors (1) and (2) and the chamber (EC) are in the respective positions 1^2, 2^2, E^2.

Step 3: Ice separation and regeneration step

After step 2, the valve V2 is opened, the valve V1 remaining open.

The components (1), (2) and (EC) move rapidly to the positions 1^3, 2^3 and C^3 at an intermediate pressure level between that of step 1 and step 2. The contents of the reactor (2) are in the decomposition position and the contents of the reactor (1) remain in the synthesis position. These synthesis/decomposition positions remain far from equilibrium, because of the thermal contact that exists between the reactors (1) and (2). As a result, the decomposition in the reactor (2) is more rapid than the synthesis that is completed in the reactor (1). Thus, condensation is immediately initiated in the device (EC), which moves rapidly to

the position C^3. This exothermic condensation is possible since the heat is absorbed by the surface melting of the pieces of ice, causing them to separate and thus making it easier for them to be subsequently removed from the device (EC). Turning the heating means (6) on in (1) right from the start of this step (at the same time as opening the valve V2) maintains the condensation in (EC), which continues to move progressively from the position C^3 to the position $C^{4'}$, again allowing gas to condense effectively. Condensation is again possible when the reactor (1) is in the position $1^{4'}$ and when the condensation pressure becomes greater than the saturation vapor pressure corresponding to the melting point T_M of the phase change material. The temperature $T_1^{4'}$ is the regeneration temperature (T_{reg}) and the device (EC) is in the position $C^{4'}$, which takes the reactor (2) to the position $2^{4'}$, again at this pressure level imposed by condensation of the gas G.

Opening valve V2 (the valve V1 remaining open) and turning on the heating means (6) in the reactor (1) triggers rapid desorption in the reactor (2), separation and removal of the ice, and the end of the synthesis in the reactor (1) followed by desorption in (1). The condensation temperature imposed at the temperature T_M by the melting of the eutectic makes it possible, on the one hand, to condense the gas G at a temperature below the ambient temperature. This allows the thermal excursion of the device (EC) to be substantially reduced, resulting in better efficiency of the method and shorter cycle times. On the other hand, the condensation pressure $P_{C4'}$ is lower than the pressure P_{C4} obtained in the case without a phase change material. This results in a decrease in the regeneration temperature of (1), and consequently that of (2), which means a reduction in the energy consumed in regenerating (1) and (2), again resulting in a better efficiency of the method and a reduction in the

cycle times.

Step 4: Cooling step and return to the initial step

5   The entire installation returns to the temperature T_0 in a shorter time if a phase change material is present, because the reactor (1) is at a lower temperature.

10   The installation according to the invention in its most general configuration, operated according to the method of the invention, thus makes it possible to achieve powerful refrigeration in very short times, which can allow the almost instantaneous production of ice for 15   example. Furthermore, when the installation contains a phase change material in the endothermic component, the regeneration temperature in the reactor operating at the highest temperature is reduced, which on the one hand shortens the duration of the process and reduces 20   the power consumption.